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The principal focus of this research program is the electronic structure aspects of nonadiabatic processes related to the stability, formation and detection of high energy density materials(HEDMs). During the current grant our work has focused on metal doped hydrogen as cyrogenic fuels. These studies were enabled by a unique system of computer codes, the BROOKLYN programs, that provide advanced capabilities for the study of the electronic structure aspects of spin-conserving and spin-nonconserving electronically nonadiabatic processes and have permitted us to make significant contributions in this area of chemistry. Our most significant algorithmic accomplishment in this grant period has been the development of algorithms for locating intersections of distinct seams of conical intersections. These algorithms proved invaluable in analyzing the seams of conical intersection in $Al+H_2$, $B+H_2$ and $C+H_2$ which are relevant to the kinetic stability of the corresponding van der Waals species in cryogenic H_2. We have also investigated the stability, and lifetime with respect to spin-nonconserving radiationless decay of the C^2D state of BAr and BNe and the B^3P state of CAr. These studies of metal rare gas bonding support the experimental work of P. J. Dagdigian on the detection of metal -rare gas complexes and the work of P. Langhoff on the spectral theory.

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PUBLICATIONS

INVITED PUBLICATIONS

1. *Molecular structure*
D. R. Yarkony, in Atomic, Molecular and Optical Physics Handbook , G. F. Drake, editor (AIP, 1996)

2. *Diabolical Conical Intersections*
D. R. Yarkony, Rev. Mod. Phys. **68**, 985 (1996)

3. *Current Issues in Nonadiabatic Chemistry* – Feature Article,
D. R.. Yarkony J. Phys. Chem. **100**, 18612 (1996)

4. *Nonadiabatic Derivative Couplings*
Encyclopedia of Computational Chemistry, editor-in-chief P. von Ragué Schleyer (John Wiley, 1998)

†5. *Conical Intersection Diabolical and Often Misunderstood*, solicited article
David R. Yarkony, Accounts of Chemical Research,31, 511-518 (1998).

6. *Diabatic potential curves and avoided crossings for diatomic molecules*
in Theoretical High Resolution Molecular Spectroscopy, editors Per Jensen and Phil Bunker, J. Wiley, to appear

7. Perspective on:*Some Recent Developments in the Theory of Molecular Energy Levels*: by H. C. Longuet-Higgins[Advances in Spectroscopy 2, 429-472 (1961)].The geometric phase effect
David R. Yarkony, Theoretical Chemistry Accounts, New century issue, submitted

JOURNAL ARTICLES

8. *Radiative and Radiationless Decay of Multichannel Resonances Resulting from Electronically Nonadiabatic Interactions: A Computational Approach Valid for both Narrow and Broad Linewidths and Large Energy Shifts*
Seungsuk Han and David R. Yarkony, Molec Phys. **88**, 53 (1996)

9. *Radiative and Nonradiative Decay of the $BH(b^3\Sigma^-)$ State:A Joint Experimental and Theoretical Study*
Xin Yang, Lisa Pederson, David R. Yarkony, and Paul J. Dagdigian, J. Phys. Chem. **100**, 5649 (1996)

10. *New and unusual bonding in open-shell van der Waals molecules revealed by the heavy atom effect: The case of BAr*
Karl Sohlberg and David R. Yarkony , J. Phys. Chem. A, 3166-3173, (1997)

11 *A Theoretical Investigation of the Spin-Orbit Induced Predissociation of BAr $C^2\Delta$*
Karl Sohlberg and David R. Yarkony, *J. Chem. Phys.* **106,** 6607-6611 (1997).

12. *The reactions $Al(^2P)+H_2 \rightarrow AlH_2(1^2A', 2^2A') \rightarrow AlH_2(X^2A_1)$ or $AlH(X^1\Sigma^+) + H$, Unusual Conical intersections and possible nonadiabatic recrossing*
Galina Chaban, Mark S. Gordon and David R. Yarkony J. Phys. Chem. A ***101,*** 7953-7959 (1997)

†13. *On the Relation Between the Bonding and the Spin-Orbit Interaction in BNe: The $C^2\Delta$* and *$1^4\Pi$ States*
Karl Sohlberg and David R. Yarkony , J. Phys. Chem. A **101**, 9520-9524 (1997)

†*14. *Systematic Location of Intersecting Seams of Conical Intersection in Triatomic Molecules: The $1^2A'$ - $2^2A'$ Conical Intersections in BH_2,*
Mark S. Gordon, Vassiliki-Alexandra Glezakou, and David R. Yarkony· J. Chem. Phys., **108**, 5657-5659 (1998)

†*15. *Unanticipated Confluences of Seams of Conical Intersection. Reinvestigating intersecting potential energy surfaces using new tools, I. $C(^3P) + H_2$*
David R. Yarkony, J. Chem. Phys., 109, 7047-7050, (1998)

16. *On the Quenching of Li (^2P) by H_2: Potential Energy Surfaces, Conical Intersection Seam, and Diabatic Bases*
Eugene S. Kryachko and David R. Yarkony, Theoretical Chemistry Accounts, **100**, 154 (1998) volume in honor of Wilfred Meyer

17. *On the Strongly Bound $B^3\Pi$ State of the CAr van der Waals Complex: Bonding and Predissociation*
Karl Sohlberg and David R. Yarkony, J. Chem. Phys., submitted

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The principal focus of this research program is the electronic structure aspects of nonadiabatic processes related to the stability, formation and detection of high energy density materials(HEDMs). During the current grant our work has focused on metal doped hydrogen as cyrogenic fuels. These studies were enabled by a unique system of computer codes, the BROOKLYN programs, that provide advanced capabilities for the study of the electronic structure aspects of spin-conserving and spin-nonconserving electronically nonadiabatic processes and have permitted us to make significant contributions in this area of chemistry. Our most significant algorithmic accomplishment in this grant period has been the development of algorithms for locating intersections of distinct seams of conical intersections. These algorithms proved

invaluable in analyzing the seams of conical intersection in $Al+H_2$, $B+H_2$ and $C+H_2$ which are relevant to the kinetic stability of the corresponding van der Waals species in cryogenic H_2. We have also investigated the stability, and lifetime with respect to spin-nonconserving radiationless decay of the $C^2\Delta$ state of BAr and BNe and the $B^3\Pi$ state of CAr. These studies of metal rare gas bonding support the experimental work of P. J. Dagdigian on the detection of metal -rare gas complexes and the work of P. Langhoff on the spectral theory.

TABLE OF CONTENTS

REPORT DEFINITION 1

SUMMARY 2

TECHNICAL REPORT 2

ACCOMPLISHMENTS/NEW FINDINGS 2

I. Characterizing novel/unexpected seams of conical intersection 2
II: Conical Intersections and Energetics Materials 3
(A) $C(^3P) + H_2$, $B(^2P) + H_2$, $Al(^2P) + H_2$
(B) $Li(^2P) + H_2$
III:Spin-nonconserving Radiationless Decay and its relation to laser characterization of HEDMs 8
(A)Unusual Bonding and the heavy atom spin-orbit effect in the open shell van der Waals $BAr(C^2\Delta)$.
(B) Extension to $BNe(C^2\Delta)$
(C) Implications
(D) $CAr(B^3\Pi)$
FUTURE DIRECTIONS 13

REFERENCES 13

REPORT DEFINITION

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PROJECT TITLE:	On the Origin of Metastability in Energetic Species
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SUMMARY

This grant period was one of considerable excitement and discovery. Our studies of Al + H_2 led us to explore novel topologies for seams of conical intersections and ultimately to develop an algorithm for identifying intersecting seams of conical intersections, our most significant algorithmic accomplishment in this grant period. This algorithm proved invaluable in analyzing the seams of conical intersection in B+H_2, C+H_2 and Li+ H_2 which are relevant to the kinetic stability of the corresponding van der Waals species in cryogenic H_2. Our C+H_2 study is particularly noteworthy since it clearly illustrated the potential pitfalls in characterizing seams of conical intersection without the above noted algorithm. We have also investigated the stability the $1^2\Delta$ state of BAr and of BNe and the $B^3\Pi$ state of CAr, and determined their lifetimes with respect to spin-nonconserving radiationless decay. These studies of metal-rare gas bonding and radiationless decay support the experimental work of P. J. Dagdigian on the detection of metal -rare gas complexes and the work of P. Langhoff on the spectral theory.

TECHNICAL REPORT

The thrust of our research program is two fold: (i) to develop computational techniques to determine the stability with respect to radiationless decay of potential high energy density materials and (ii) to use of those techniques to study chemically relevant systems and assess the feasibility of their spectroscopic characterzation/detection. During the current grant have developed new tools for the study of nonadiabatic processes. In addition to their use in accessing the stability of energetic materials these algorithms have potentially broad impact in the field of nonadiabatic chemistry. Below we discuss the most significant components of our current research effort.

ACCOMPLISHMENTS/NEW FINDINGS

I. Characterizing novel/unexpected seams of conical intersection

As part of our Air Force sponsored research we have used the criterion[1] $\mathbf{g}^{IJ}(\mathbf{R}_X) \times \mathbf{h}^{IJ}(\mathbf{R}_X) \equiv \mathbf{t}^{IJ}(\mathbf{R}_X) = \mathbf{0}$ where $\mathbf{R}_X$ is a point on a C_{2v} seam of conical intersection to establish the existence of a C_s seam intersecting the C_{2v} seam at $\mathbf{R}_X$. Here

$$2g_\tau^{IJ}(\mathbf{R}) \equiv \left(\mathbf{c}^I(\mathbf{R}_x) - \mathbf{c}^J(\mathbf{R}_x)\right)^\dagger \frac{\partial \boldsymbol{H}(\mathbf{R})}{\partial \tau}\left(\mathbf{c}^I(\mathbf{R}_x) + \mathbf{c}^J(\mathbf{R}_x)\right) \qquad (1a)$$

$$h_\tau^{IJ}(\mathbf{R}) \equiv \mathbf{c}^I(\mathbf{R}_x)^\dagger \frac{\partial \boldsymbol{H}(\mathbf{R})}{\partial \tau}\mathbf{c}^J(\mathbf{R}_x), \qquad (1b)$$

$$\left[\boldsymbol{H}(\mathbf{R}) - E_I(\mathbf{R})\right]\mathbf{c}^I(\mathbf{R}) = \mathbf{0} \qquad (1c)$$

$\boldsymbol{H}(\mathbf{R})$ is the electronic hamiltonian matrix, and $E_I(\mathbf{R}_x) = E_J(\mathbf{R}_x)$. It is important to note that $\mathbf{g}^{IJ}(\mathbf{R}_X) \times \mathbf{h}^{IJ}(\mathbf{R}_X)$ is readily evaluated using analytic gradient techniques in algorithms we have developed.[2] This approach will be particularly valuable in general polyatomic molecules (> 3 atoms) where the seam of conical intersection is a surface. In such situations, in the absence of this criterion, it would be difficult to distinquish between intersecting seams and the dimensionally allowed continuation of a the seam into regions of reduced symmetry.

II:Conical Intersections and Energetics Materials

(A) $C(^3P) + H_2$, $B(^2P) + H_2$, $Al(^2P) + H_2$

The reactions

$$M(^{2S+1}P) + H_2 \rightarrow MH_2(1^{2S+1}A_i,\ 1^{2S+1}B_{i'}) \rightarrow MH_2(^{2S+1}Y) \qquad (2a)$$

$$\rightarrow MH(X^1\Sigma^+) + H \qquad (2b)$$

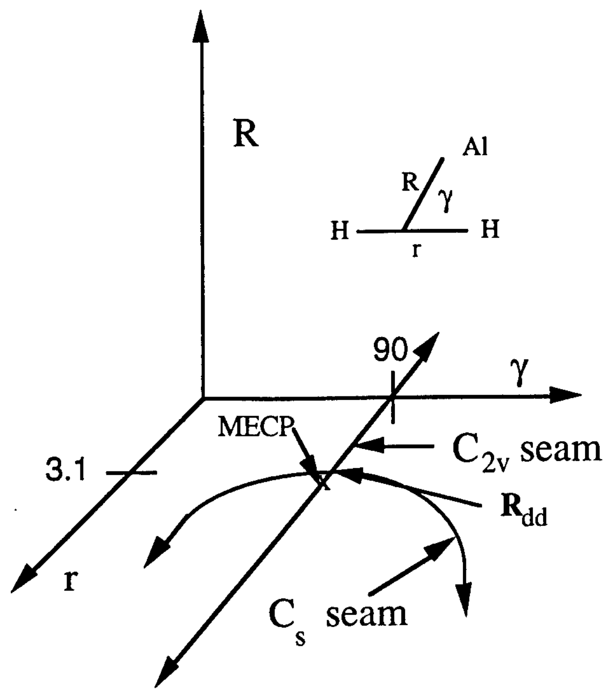
where (2S+1, i, i',Y) = (2,1,2,A_1) for aluminum[3] and boron[4] and (2S+1, i, i', Y) = (3,2,1, B_1) for carbon,[5] are relevant to the stability and properties of M doped cryogenic hydrogen. The formation of the dihydride $MH_2(^{2S+1}Y)$, channel (2a), could limit the stability of the van der Waals complex M — H_2 that constitutes the energetic material, while channel (2b) may be involved in the combustion of the energetic material.

Low energy pathways to the dihydride(a $^2A_1$ state for aluminum and boron and a $^3B_2$ state for carbon) involve the $^2B_1$ section of the $1^2A'$ PES for aluminum and boron and the $^3A_2$ section of the $1^3A''$ PES for carbon. Thus the C_{2v} constrained minimum energy pathway to the dihydride, T-shaped approach of M to H_2, procedes over the ridge corresponding to the symmetry-allowed $^{2S+1}B_i - {}^{2S+1}A_{i'}$ seam of conical intersection. The minimum energy crossing point (MECP), the minimum energy point on the $^{2S+1}B_i - {}^{2S+1}A_{i'}$ seam, is the transition state for this path. However there are <u>two</u> directions perpendicular to the ridge one that preserves C_{2v} symmetry, the aforementioned constrained reaction path, and an asymmetric mode that removes the C_{2v} symmetry. Displacements along this mode give rise to general C_s geometries which conventionally, would be devoid of conical intersections, and would include the true transition state. In fact the transition state for these systems is found quite near the MECP which therefore provides a useful upper bound to the barrier for forming the dihydride.

The MECP for the BH_2 $1^2A' - 2^2A'$ conical intersection seam was found to be approximately 0.6eVabove the B + H_2 asymptote. This result, which is less than half the value in AlH_2, represents a considerable lowering of a previous estimate[6] of the insertion barrier and thus has potentially important implications for the stability of B doped cryogenic hydrogen. For CH_2 the MECP on the $^3A_2 - {}^3B_1$ C_{2v} seam of conical intersection was found to be only 0.77 kcal/mol above the $C(^3P)$ + H_2 asymptote. Thus the barrier for the van der Waals complex $\rightarrow$ dihydride conversion is at best small.

These results are of considerable practical importance. Yet they may not be the most influential results of these study. The figure below[7] presents a schematic representation of the $1,2^2A'$ seam in $Al(^2P)H_2$ reporting $\mathbf{R}_x(r) = (R(r), r, \gamma(r))$ for which $E_{1^2A'}(\mathbf{R}_x(r)) = E_{2^2A'}(\mathbf{R}_x(r))$, that is the locus of points on the $1^2A'$ - $2^2A'$ seam of conical intersection using Jacobi coodinates,

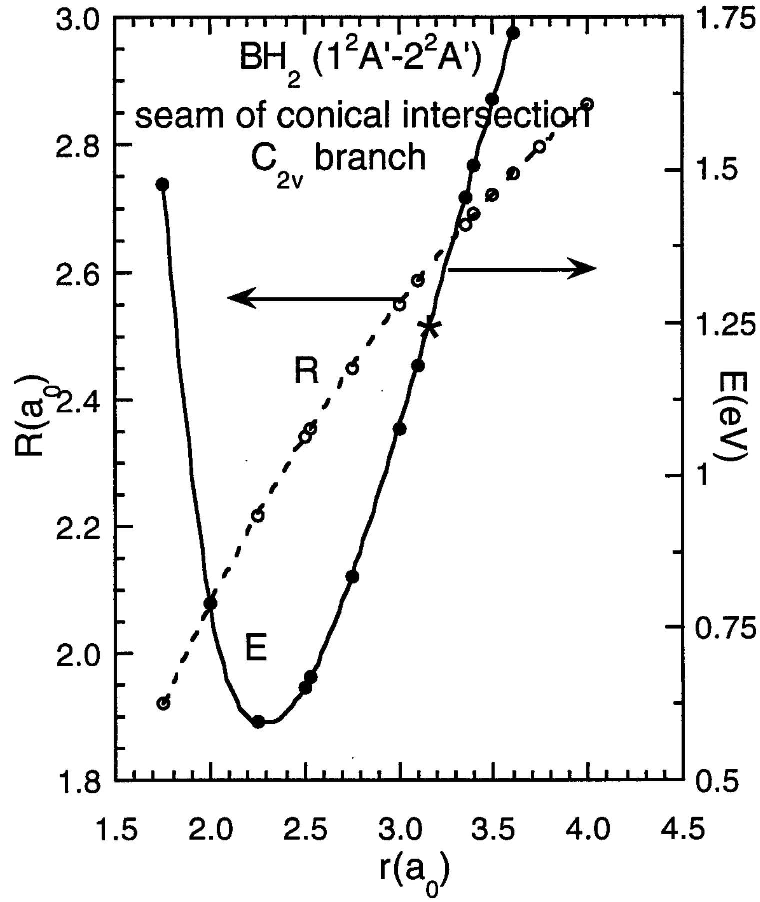
$\mathbf{R} = (R, r, \gamma)$ with r as the seam parameter. It would be expected that $\gamma(r) = 90°$ for all r, that is the seam should have C_{2v} symmetry. However this is plainly not the case! For $r < \sim 3.1a_0$, $\gamma(r) \equiv 90°$ as expected.



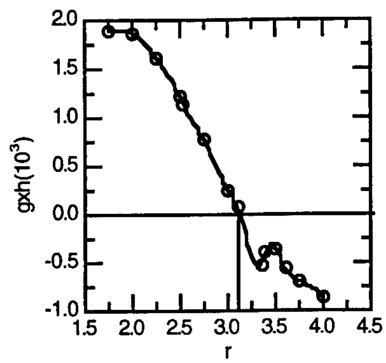
However for each $r > \sim 3.1a_0$ there are three points of conical intersection. One point has $\gamma = 90°$ and is part of the C_{2v} seam. There are also two equivalent points with $\gamma = \gamma_x$, $180° - \gamma_x$ having only C_s symmetry. It is important to emphasize that all $\mathbf{R}_x$ are on the $1^2A'$ - $2^2A'$ seam of conical intersection. This unusual feature represents a trifurcation of the C_{2v} seam as r increases past $\sim 3.1a_0$. Equivalently it is the intersection of a C_s seam and a C_{2v} seam at the C_{2v} point $\mathbf{R}_{dd}$. Since points of conical intersection are referred to as diabolical points,[8] points at the intersection of two seams of conical intersection are referred to as doubly diabolical points.[1]

The importance of this feature cannot be overemphasized. Its existence means that the significant nonadiabatic effects associated with conical intersections cannot automatically be assumed to exist only for nuclear configurations yielding symmetry-allowed intersections. Additional confluences are possible in unexpected regions of nuclear coordinate space and may result in 'confluences of confluences'.

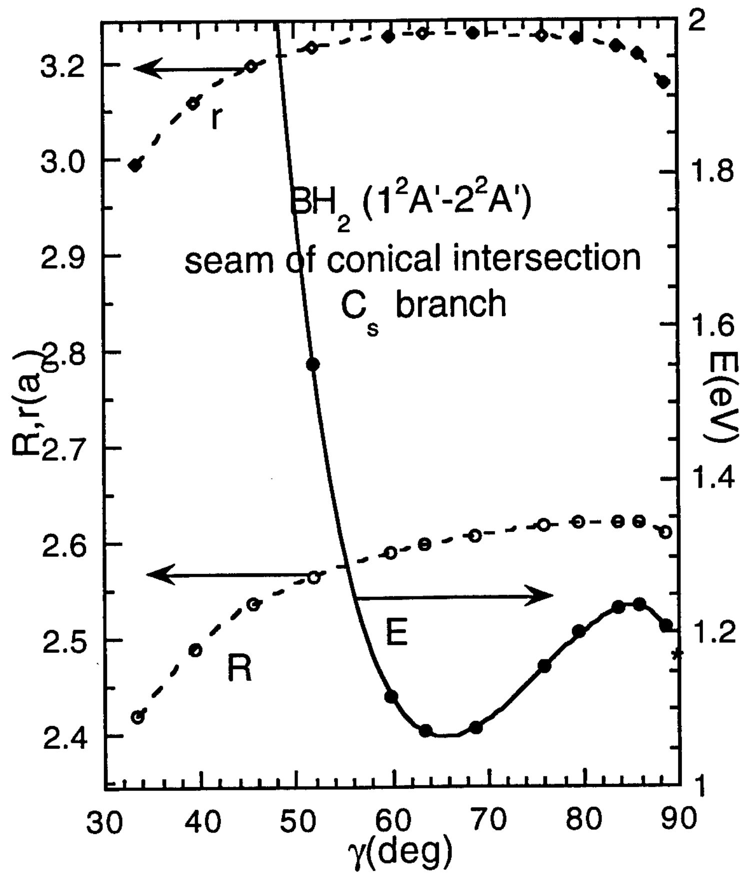
In view of the Al(^{2}P)-H_2 result it was natural to ask whether a similar result would be obtained in the B-H_2 and C - H_2 systems. The C_s seam in AlH_2 was located quite serendipitously. The criterion described in section I allowed us to <u>anticipate</u> the existence of the C_s seam given only knowledge of the (standard) C_{2v} seam. The following two figures[4] consider the BH_2 $1^2A'$-$2^2A'$ seam of conical intersection. The first figure presents $\mathbf{R}_x(r) = (R(r), r, \gamma(r) = 90)$ and $E_{1^2A'}(\mathbf{R}_x(r)) = E_{2^2A'}(\mathbf{R}_x(r))$ relative to B(^{2}P) + H_2. This is a standard C_{2v} seam of conical intersection between a $^2A_1$ and a $^2B_2$ state.



However as the following figure shows $\mathbf{g}^{IJ} \times \mathbf{h}^{IJ}$ vanishes near $r = 3.1a_0$ (* point above)



Thus an intersecting C_S branch of the seam is expected at $\mathbf{R}_x(r\sim3.1)$. The following figure presents that intersecting branch, $\mathbf{R}_X(\gamma) = (R(\gamma), r(\gamma), \gamma)$ and $E_{1^2A'}(\mathbf{R}_X(\gamma)) = E_{2^2A'}(\mathbf{R}_X(\gamma))$.



The above result, published as a communication in the Journal of Chemical Physics, demonstrates the power of this approach as a general tool for locating intersecting seams of conical intersection.[4]

While these results were quite unexpected perhaps the most fundamentally surprising result to emerge these studies was the demonstration that for CH_2 in addition to the conventional C_{2v} and $C_{\infty v}$ seams of conical intersection, there again exists a C_s seam of conical intersection that in turn intersects the C_{2v} seam. This result was unexpected since for CH_2 the C_{2v} (and $C_{\infty v}$) seams of conical intersection had been carefully studied by Harding, Schatz and coworkers[9,10] as part of a determination of global $1,2^3A''$ PESs based on 6000 high quality *ab initio* points! For this reason the CH_2 results appeared as a communication in J. Chem. Phys.[5] The CH_2 results are expected to be particularly important since the MECP on the C_s portion of the seam as exoergic relative to the $CH(X^2\Pi) + H(^2S)$ asymptote.

The trifurcation exhibited by CH_2, BH_2 and AlH_2 is highly nonstandard it was important to ask how it could be demonstrated that the C_s seam of conical intersection represents a true intersection seam rather than narrowly avoided crossings. One could determine whether in fact these points are points of conical intersection by considering the phase of the electronic wavefunctions for closed paths C surrounding the point. However this can be quite tedious. We have shown[11] that $X(C_\rho)$, the circulation of the derivative coupling, $\mathbf{f}^{IJ}(\mathbf{R})$, where $f_\tau^{JI}(\mathbf{R}) = \langle \Psi_J(\mathbf{r};\mathbf{R}) | (\partial/\partial\tau)\Psi_I(\mathbf{r};\mathbf{R}) \rangle_r$ and τ is an internal coordinate, along a small loop of radius ρ around the point in question, C_ρ, can be used to consider this question since:

$$X(C_\rho) = \oint_{C_\rho} \mathbf{f}^{IJ}(\mathbf{R}) \cdot d\mathbf{R} \xrightarrow[\rho \to 0]{} \kappa\pi \qquad (3)$$

where $\kappa = 0(1)$ if $0(1)$ conical intersections are enclosed in C_ρ. This approach has the advantage that the phase of the integrand at the endpoint of the loop is known, since $\mathbf{f}^{IJ}(\mathbf{R})$ does not change sign after traversing a closed loop. This provides a useful control in assigning the phase of the integrand at neighboring points. The existence of three independent components for the derivative coupling vector $\mathbf{f}^{IJ}(\mathbf{R})$ can also help to decide phase relationships in otherwise ambiguous situations without the need to determine additional points. The use of eq. (3) is made

computationally tractable by an algorithm we have developed[12,13] for the efficient evaluation of the $\mathbf{f}^{IJ}$ using analytic gradient techniques.

Eq. (3) was used to confirm that for AlH_2, BH_2 and CH_2 the $1,2^{2S+1}A$ potential energy surfaces do in fact exhibit this remarkable, and heretofore virtually unknown, locus of seams of conical intersection (the only other reports based on *ab initio* wavefunctions are for the $1^1A'$ and $2^1A'$ states of O_3[14] and the $2^3A''$ and $3^3A''$ states of CH_2[15]).

(B) $Li + H_2$[16]

The ultimate fate of excited $Li(^2P)$ in cryogenic H_2 matrices is relevant to the quantitative detection of ground state $Li(^2S)$ in this matrix. The quenching of electronically excited alkali metal atoms has been found by Scoles and coworkers[17] to be extremely efficient. Fajardo's group has also studied this quenching process. We have investigated the $1^2A'$ - $2^2A'$ conical intersection seam in LiH_2. These states correlate with $Li(^2S)+H_2$ and $Li(^2P)+H_2$ so that this seam is principally responsible for this quenching.[18,16] We have again demonstrated the existence of a previously unknown portion of this seam with C_s symmetry that intersects the C_{2v} seam. This results is quite surprising in view of the long history of theoretical study of these states (see references in Ref. 16).

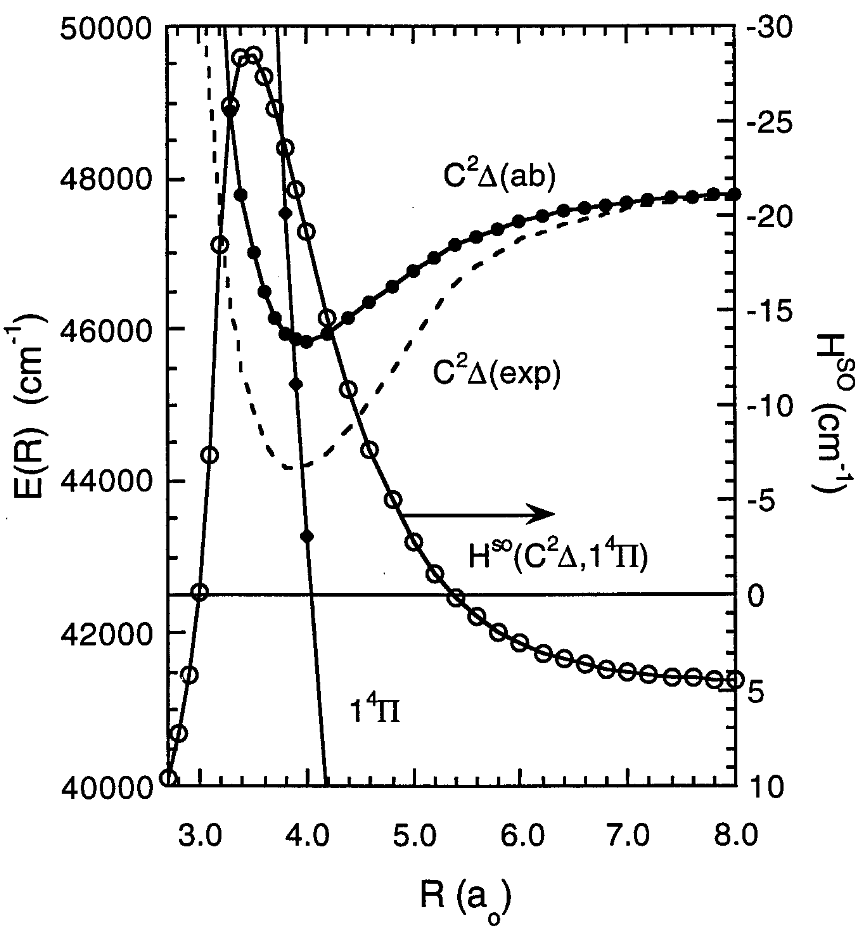
III:Spin-nonconserving Radiationless Decay and its relation to Laser Detection of HEDMs

A.Unusual Bonding and the heavy atom spin-orbit effect in the open shell van der Waals BAr

The importance of boron doped in cryogenic hydrogen matrices to the cryogenic fuels program lead Dagdigian and coworkers to systematically study the interactions of the open shell van der Waals molecules formed by boron in its electronic ground, or excited, state with a rare gas or molecular hydrogen.[19-23] That research suggested that the $C^2\Delta$ state of BAr is quite strongly bound but is rapidly predissociated by spin-orbit induced coupling to the repulsive $1^4\Pi$ state.[23] The later observation seemed counterintuitive since spectroscopic studies suggested the open shell moiety to be a largely unperturbed boron atom which has at best modest spin-orbit interactions. For this reason we considered the electronic structure of the $C^2\Delta$ and $1^4\Pi$ states of BAr and the spin-orbit interactions that couple these states. The results of this study[24] were quite surprising

and had important implications for a long standing controversy[25] concerning the anomalous fine structure splitting in alkali metal - rare gas dimers[26] and for other AFOSR research efforts, including M. Duncan's work at the University of Georgia on metal ion-rare gas interactions[27] and P. W. Langhoff's work on spectral theory.[28]

The computational treatment was particularly challenging owing to the need to treat near-degeneracy effects attributable to the Rydberg $1s^2 2s^2 3d^1\ {}^2D$ electron configuration. The results of the electronic structure treatment, which are pictured below, confirm[$C^2\Delta$(ab)][24] the unusually strong binding in the BAr $C^2\Delta$ electronic state observed by Dagdigian[$C^2\Delta$(exp)].



More significantly however it emerged that the predissociation of the $C^2\Delta$ state[29] was a consequence of the heavy atom effect on the $C^2\Delta - 1^4\Pi$ spin-orbit coupling, $H^{so}(C^2\Delta, 1^4\Pi)$. The large increase in $H^{so}(C^2\Delta, 1^4\Pi)$ near the $C^2\Delta$ equilibrium geometry seen in the above figure represents the heavy atom effect, the borrowing of spin-orbit coupling by boron from argon. The marked increase of $H^{so}(C^2\Delta, 1^4\Pi)$ with decreasing internuclear separation suggested nonnegligible overlap between valence orbitals on argon and boron which lead us to establish a novel origin for the bonding in the $C^2\Delta$ state - see below.

(B) Extension to BNe($C^2\Pi$)

We extended this work to the $C^2\Delta$ state of BNe. Dagdigian and coworkersrecorded the BAr[23] and BNe[30] laser fluorescence excitation spectra and the BAr fluorescence depletion spectra in the region of the atomic boron $2s2p^2\ ^2D \leftarrow 2s2p\ ^2P$. The $C^2\Delta$ state of BNe was found to fluoresce but that of BAr did not. The absence of radiative decay in BNe($C^2\Delta$) suggests predissociation by a repulsive $^4\Pi$ state. To help interpret these results we performed computational studies to determine the mechanism, and rates, of BNe($C^2\Delta$, v) predissociation. The potential energy curves for both the $C^2\Delta$ state and the repulsive $1^4\Pi$ state, and the spin-orbit interactions that couple these states were determined and used to compute the radiationless decay rates. Combined with the above BAr results these calculations provide a conceptually clear picture, and quantitively reliable treatment, of the BRg ($C^2\Delta$,v) predissociation.[29,31,24]

(C) Implications

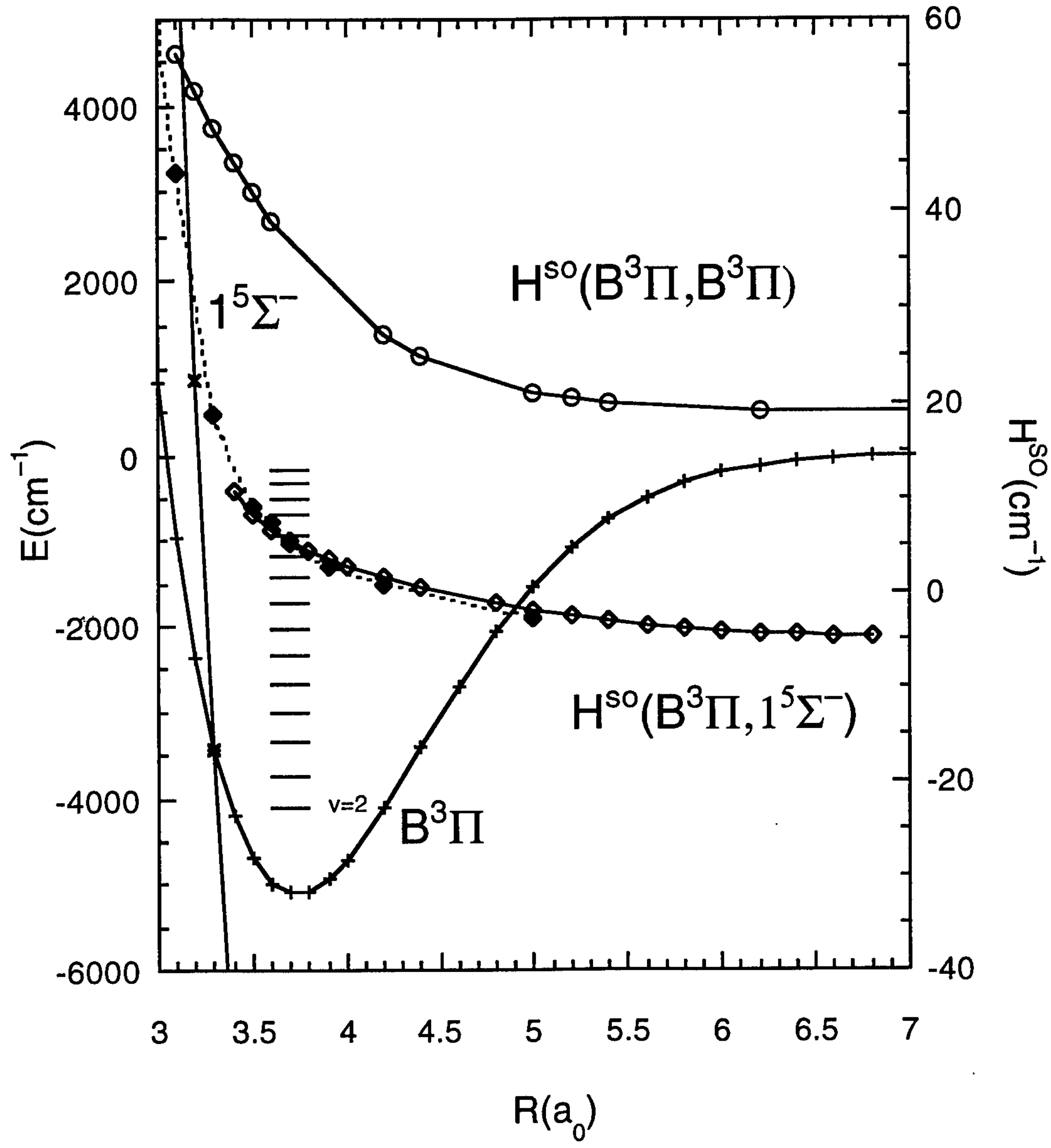
While the BRg ($C^2\Delta$,v) predissociation rates are of practical significance to the the HEDM program perhaps the most important outcome of these studies are the generalizable insights concerning the connection between the bonding in these species and the heavy atom effect, the later being principally responsible for the BRg ($C^2\Delta$,v) predissociation. The orbital overlap that leads to the heavy-atom effect in the spin-orbit coupling $1^4\Pi \sim C^2\Delta$, gives rise to overlap of a vacant axial M orbital and the highest occupied axial orbital on Rg. Pursuing this line of reasoning we showed that the strong binding is best described as a dative, or coordinate covalent, bond with the Ar furnishing the electrons from its fully occupied $3p_z$ orbital to an empty B $2s2p_z$ hybrid orbital.

Overall the binding results from a balance of this bonding interaction and electron correlation effects, with high-order configuration interaction effects being very important in describing the overall binding. Since a spectral theory treatment of bonding in metal-rare gas van der Waals complexes depends on accurate knowledge of the pairwise interactions of both the ground and excited electronic states[28] this finding has important implications for P. W. Langhoff's spectral representation work.

On the basis of this analysis we were able to explain[26] the fine structure splitting in the $^2\Pi_\Omega$ states of Li(2p)Ne and Li(2p)Ar , which had been a matter of considerable debate.[25] It had been previously been asserted[25] that mixing of Rydberg states on the rare gas with metal valence states accounted for the observed heavy atom effect. However our model of the bonding indicated that valence orbitals on the rare gas should be responsible for the observed effect. We were subsequently able to show[26] that the heavy atom effect was in fact attributable to valence orbitals on the rare gas. These notions are also relevant to the fine structure splittings in *eg.* the MgRg and MgN_2 complexes studied by Professor M. Duncan as part of his AFOSR sponsored work at the University of Georgia.

(iv) CAr

Finally we considered the $B^3\Pi$ state of CAr.[32] This state is potentially of use in a laser induced fluorescence detection scheme for the van der Waals complex CAr($X^3\Sigma^-$). It is however predissociated by the $^5\Sigma^-$ state correlating with C($1s^22s2p^3$). The figure below summarizes our electronic structure results.



The $B^3\Pi$ state is quite strongly bound for a van der Waals complex, with binding energy ~5000cm^{-1}! The bonding and existence of a clear heavy atom effect in the $^5\Sigma^-$ ~ $B^3\Pi$ spin-orbit interaction are consistent with the dative bonding model noted above. We find that spin

nonconserving predissociation of the the $B^3\Pi$ state will not preclude use of the $B^3\Pi$ state to detect the ground $X^3\Sigma^-$ state although Franck-Condon factors limit the vibrational levels of the $B^3\Pi$ state that are accessible in practice.

Future Directions

As part of our renewal proposal we will work with David Weeks of AFIT on the

$$B+H_2 \rightarrow BH + H$$

scattering problem. We are in the process of generating the $1,2^2A'$ potential energy surfaces and the derivatve couplings. An approximate transformation to diabatic states is being developed 'on the fly' based on our analysis which shows the transformation in question necessarily removes all the singularity in the derivative coupling.[33] It is important to observe that this approach is capable of handling the trifurcation of the C_{2v} seam of conical intersection described above. Given the novel seam of conical intersection in this system these potential enegy surfaces and the subsequent dynamical studies should be of general interest for the field of nondiabatic dynamics as well as of practical concern in the HEDM program.

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